Interactions among solid, liquid and vapor phases in impact events : implications for the early Earth environments and origin of life

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論 文 内 容 要 旨

Abiotic formation of biomolecules on the early Earth was an essential requlrement for origin of life. Such prebiotic formation has been a research subject for many previous investigators. It was believed "already-solved" problem for last several decides largely based on the Urey−Miller's experiments. Miller successfully synthesized various biomolecules from reducing gas mixture which atmospheric methane and ammonia are assumed as sources of carbon and nitrogen for the organic syntheses. However, recent studies on the early Earth demolished the fundamental assumption of the "already-solved" problem : Slightly oxidized atmosphere contains carbon dioxides and nitrogen. Rebuilding and reformation of the prebiotic organic formation adapted to the new assumptions are required.

Supply of biomolecules by carbonaceous chondrites is a preferred model for many previous investigators. Carbonaceous chondrites confidently contain several kinds of biomolecules. However, types of amino acids in twenty-protein-constituent amino acids are limited in the meteorite. Types of nucleic acid bases are also limited in the meteorites. In addition, skepticism presents if these organic molecules in carbonaceous chondrites could survive from the impact to ocean ; thermal decompositions would be more likely. Therefore, we need to consider other possibilities and/or geological events for origin of biomolecules on the early Earth.

In order to synthesize organic molecules on the early Earth using atmospheric carbon and nitrogen species, reducing reagents are inevitable. The ancient volcanic rocks, normal oceanic basalts and/or komatiites, are considered to be reducing agents by many previous investigators because they contain ferrous iron. In this model, water-rock interactions between these ancient rocks and sea water, thus submarine hydrothermal activities, responsible for organic synthesis using carbon and nitrogen species in directly derived from the ancient atmosphere. Some experimental studies simulating submarine hydrothermal conditions were performed previous investigators and successfully synthesized hydrocarbons. In addition, productions of several hydrocarbons are found in a present submarine hydrothermal vent. However, there is so far no research which suuccessfully synthesized biomolecules in simulated hydrothermal conditions, producing skepticism if

submarine hydrothermal environments were suitable for prebiotic bioorganic synthesis.

Meteorite impact models have been proposed by several researchers as an initiation process of the chemical evolution. Dr. Nakazawa, one of supervisors of the present study, proposed ocean impact hypothesis for the synthesis of bioorganic molecules on the early Earth. Because certain meteorites contain metallic iron and carbon, their interactions with oceanic water and atmospheric nitrogen during shock and post shock events may produce organic molecules. The point or uniqueness of this idea is introduction of iron and carbon into the reaction system : both behave as reducing agents and carbon behaves as carbon sources for organic molecules. Heavy bombardments of meteorites between 3.8-4.0 billion years ago, where the Earth is thought to have been prebiotic, are suggested by lunar crater records. Therefore, the primary purpose of the present thesis study is set to demonstrate the ocean impact event in the laboratory, and then examine if such events could connect the production of import ant biomolecules.

In chapter 1, the historical backgrounds of classical organic molecule syntheses, environments on the early Earth, organic molecules in meteorites, modern organic molecules synthesis simulating early Earth, and impact events of meteorite were reviewed.

In chapter 2, interactions among meteoritic minerals and water by impact reactions focused on mineralogical aspects are described based on the result of shock−recovery experiments and mineral analyses with electron microcopies. Ultrafine particles of olivine and metal oxides were experimentally synthesized from olivine, metals, and water using shock wave. Water changed its phase to supercritical by a shock wave traversal. The presences of these particles and phase change of water suggest that reactions went through the dissolution and precipitation in and from the supercritical water respectively. Serpentine, a kind of phyllosilicates, was also formed through the water-mineral interactions by shock wave. The impact-synthesized ultrafine particles and phyllosilicates might have influenced environments on the early Earth such as sun flux to the Earth's surface. In addition, the phyllosilicate formation in present study also suggests origin of phyllosilicates in comets because phyllosilicates are thought to be difficult to be synthesized in comet ice.

In chapter 3, interactions among meteoritic minerals and water by impact reactions focused on organic chemical reactions are described based on the result of shock-recovery experiments and analyses of organic products with LC/MS and GC/MS. In this synthesis ^{13}C was used as the carbon source for clear identification between experimental products and contaminations. Several kinds of carboxylic acids and amines were formed by impact chemical reactions among iron, nickel, water, carbon, and nitrogen. Glycine was synthesized in addition to carboxylic acids and amines when ammonia solution was added in the starting material. These results suggest that impact of iron-bearing meteorite, mainly ordinary chondrite, to prebiotic ocean produce large variety and amount of bioorganic molecules on the early Earth, Such biomolecules might have preceded further chemical evolution depositing on seafloor with impact-synthesized phyllosilicates.

論文審査の結果の要旨

初期地球環境でのアミノ酸生成は、生命起源に関する未解明の大問題である。古川善博は、初期地球における後期隕石重爆撃によって最初の有機分子が生成されたとするアイディアのもと各種実験を行い、そのアイディアが正しいことを実証した。まず、初期地球における後期隕石重爆撃を実験室で再現するために、物質・材料研究機構で衝撃圧縮実験を展開した。従来、水を含んだ系での衝撃回収実験は不可能とされてきた。しかし、古川善博の新たな工夫により、衝撃圧縮環境での水－鉱物反応実験を世界ではじめて可能にした。その結果、難溶性のケイ酸塩鉱物が、1秒以下の短い時間に超臨界水に溶解し、再結晶することが明らかになった。再結晶化した鉱物は煙微粒子としての性質を有することを見いだした。それと同時に、鉄酸化物煙微粒子など形成され、水－鉱物反応が酸化還元反応を伴う現象であることを示した。これら成果は ISI 誌に既に出版されている。

更に、同一の実験において含水鉱物が容易に生成されることを示した。従来、含水鉱物生成には水の拡散を許すのに十分な反応時間が必要とされていた。しかし、衝撃圧縮実験では、機械的な初生鉱物の破壊と水の拡散が相互作用し、1秒以内に十分な活性化エネルギーが確保され、含水鉱物が生成されることを示した。この新しい知見は、初期地球で起こった隕石重爆撃において多量に含水鉱物が形成されたとする考えを導いている。それだけでなく、宇宙空間で彗星どうしが衝突した時なども容易に含水鉱物が形成されることをも示している。太陽系に於ける惑星形成時の水の運搬を理解する上での重要な成果を得た。この成果は現在 ISI 誌で査読中である。

本論文の主となる部分が、炭素を上記実験系に含ませて、世界で初めて衝撃圧縮環境で有機分子合成に成功したことである。炭素源として炭素13を用い、最先端技術である LC－MS を用いて、炭素13からなるアミノ酸、カルボン酸、アミンなど，の生体有機分子の生成されたことを実証した。生命発生前の地球に、いかにして生体有機分子を用意するか不明であったが、本実験の成果により、新しい生命起源説を提示するに至った。この成果は Nature（geoscience）に出版された。

以上の古川善博の研究成果は、自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって，古川善博提出の博士論文は，博士（理学）の学位論文として合格と認める。